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(54) SEPARATOR FOR STORAGE BATTERIES

(71) We, YUASA BATTERY COMPANY LIMITED, a Japanese Corporation, of 6-6 Johsaicho, Takatsuki City, Osaka Prefecture, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a separator for storage batteries and more particularly sealed lead-acid storage batteries.

Various kinds of separators made of glass fibres are already well known, for example, from U.S. Patent No. 3,862,861. However, they have proved most unsatisfactory for sealed lead-acid storage batteries. For example, in a sealed lead-acid storage battery, the amount of electrolyte must not be so excessive as to be fluid but a limited amount of electrolyte must be retained in the micropores of a glass fibre separator, otherwise, due to the generation of oxygen and hydrogen following charging the electrolyte will leak out or cease to increase the concentration so adversely affecting the performance and life of the storage battery. It is therefore desirable for the separator to retain sufficient electrolyte and have a large number of small micropores. Further, it is important that the separator be strong enough to permit handling during assembly of the storage battery. It is also desirable to manufacture the separator as cheaply as possible.

With the aim of avoiding the disadvantages of conventional separator and of achieving the above desiderate, we propose, in accordance with the present invention a separator for storage batteries in the form of a sheet made by entangling together first glass having a diameter smaller than 1 micron as a base and second glass fibres having a diameter larger than 1 micron and an average fibre length of at least 5 mm.

Embodiment of the invention will now be described by way of example, with reference to the accompanying drawings in which:-

Figure 1 shows a part (much enlarged) of a separator for a storage battery containing various kinds of glass fibres having different diameters.

Figure 2 is a graph showing the tensile strength of various kinds of separator for storage batteries consisting of glass fibres having a diameter larger than 1 micron, as a function of the average fibre length.

Figure 3 is a graph similar to Figure 2 showing the shape recoveries of various kinds of separators for storage batteries.

The separator for storage batteries of the present invention is in the form of a sheet made by entangling together first glass fibres having a diameter smaller than 1 micron as a base and second glass fibres having a diameter larger than 1 micron and having an average fibre length of at least 5 mm or larger.

In the preferred embodiment, the separator consists of 50 to 95% by weight of first glass fibres and 50 to 5% by weight of second glass fibres. A separator consisting of only fine glass fibres having a diameter smaller than 1 micron, is most suited for sealed lead-acid storage batteries but has comparatively poor mechanical strength and therefore is not easy to handle, so making it difficult to assemble the storage battery. Also such fine glass fibres are very costly. By mixing with these first fibres, fibres having a diameter larger than 1 micron, a cheap separator having a very much improved mechanical strength can be obtained. However, the amount of glass fibres smaller than 1 micron is preferably 50 to 95% by weight (of the weight of the entire separator). When the amount is less than 50% by weight the microporosity of the separator will be lost, the amount of the retained electrolyte

and electrolyte retention is reduced to such an extent as to make the separator unsuitable for sealed lead-acid storage batteries. On the other hand, when the amount is more than 95% by weight, the separator is costly to produce and has poor mechanical strength, since the amount of the glass fibres thicker than 1 micron is too low.

It is advantageous for the larger second fibres to include or to be 10 to 30 microns in diameter since such fibres are not only cheap but also impart greater mechanical strength and shape recovery of the separator for storage batteries. Further, in order to further improve the mechanical strength, the separator may also contain organic fibrous materials or a binding material may be deposited on the glass fibres, prior to forming the sheet. In such case, the organic fibrous materials may be synthetic resin fibres, for example, polyester, polypropylene or acrylonitrile or natural fibres such as cellulose fibres. These latter natural fibres are preferred in that they are high in the dispersibility, have many branches and are easy to entangle. Further, if the amount of the organic fibrous materials is less than 0.1% by weight, there will be no reinforcing effect. Amounts greater than 5% by weight, tend to reduce the electrolyte retention making the separators unsuitable for storage batteries. Therefore, the range of 0.1 to 5% by weight is preferred. When the separator is formed of glass fibre, on which a binding material is deposited prior to forming the sheet and other glass fibres without binding material are entangled therewith so that the two groups of fibres become bonded together, the mechanical strength of the resulting separator is much improved. In such case, not only vegetable oils and fats such as linseed oil and cotton seed oil but also animal oils and fats and phenol-formaldehyde resins can be used as the binding material. However, vegetable oils and fats, particularly, semi-drying oils and drying oils are preferred because these produce better dispersion of the fibres in water and the film forming ability, fibre binding ability and price are favourable.

Further, the glass fibres on which binding material is to be deposited may be of any diameter.

The amount of the glass fibres to be treated with the binding material is preferably 0.1 to 40% by weight, because, if it is less than 0.1% by weight, there is no improvement in the mechanical strength of the separator and, if it is more than 40% by weight, the properties essential for sealed lead-acid storage batteries (i.e. the ability to absorb and retain the electrolyte) are impaired.

Restricting the average length of the second glass fibres (diameter larger than 1 micron) to at least 5 mm or larger, it has an advantage of greatly improving the mechanical strength and shape recovery as of a separator for storage batteries. If the average fibre length is less than 5 mm, the number of the fibres entangled with the other fibres will decrease and the reinforcing effect will remarkably reduce.

The present invention will now be described in more detail in the following with reference to specific examples:

Example 1

70% by weight of glass fibres having a diameter of 0.5 micron and 30% by weight of glass fibres cut to a length of 10 mm and having a diameter of 11 microns, are uniformly dispersed at a rate of 0.5 part by weight to 100 parts by weight of water, are sheet-formed by conventional paper making methods and are dehydrated and dried to obtain a storage battery separator. A separator made in this way was tested and compared with a conventional storage battery separator, made using glass fibres thinner than 1 micron, the results being shown in Table 1. It will be seen that both separators meet the requirements of a sealed lead-acid storage battery but that the separator of the present invention is far superior to the conventional separator, particularly in its mechanical strength and shape recovery.

TABLE 1

Characteristics	Separator of the present invention	Conventional separator
Maximum pore diameter (microns)	19.0	23.0
Tensile strength (kg/cm^2)	9.8	2.5
Amount of retained electrolyte (H_2SO_4 c.c./dry sepa. c.c.)	2.9	3.1
Electrolyte retention (%)	97	95
Shape recovery (%)	95	70

Notes:

1. Maximum pore diameter

The maximum pore diameter of the separator of the present invention is smaller than of the conventional separator and shows that the separator of the present invention has a comparatively small pore diameter and is very effective to prevent short-circuiting when arranged between positive and negative plates.

2. Tensile strength

The Tensile strength is shown as a mechanical strength. The separator of the present invention is about 4 times as high as the conventional one in the tensile strength and shows that it is very easy to handle in assembling storage batteries.

3. Amount of the retained electrolyte

A test piece of the separator is dipped in an electrolyte consisting of sulphuric acid of a specific gravity of 1.30 and withdrawn. After the lapse of 5 minutes, the amount of the electrolyte and the volume of the separator as dried in the test piece are measured. The amount of the retained electrolyte is a value obtained by dividing the former by the latter. The separator of the present invention is not so different from the conventional one in the amount of the retained electrolyte and proves well suited to sealed lead-acid storage batteries.

4. Electrolyte retention

A test piece of the separator is dipped in an electrolyte consisting of sulphuric acid of a specific gravity of 1.30, is withdrawn and held under an acceleration of 6G for 30 seconds and then the amount of the electrolyte remaining in the test piece and the initial amount of the electrolyte before the test are measured. The electrolyte retention is a value showing in (% terms) the rate of the former to the latter. The separator of the present invention is better able to retain electrolyte than a conventional separator and proves most suitable for use in a sealed lead-acid storage battery, even when subject to external vibrations and shocks.

5. Shape recovery

First, the thickness T_1 of the test piece of the separator under a load of 5 kg/dm^2 was measured. Then a load of 20 kg/dm^2 was applied to the test piece for 1 minute, the shape recovery being indicated (in % terms) by dividing T_2 by T_1. The separator of the present invention is better in this respect than a conventional separator. As is well known, a battery element consisting of positive and negative plates and separators is held in a battery under pressure but, if the shape recovery of the separator is poor, no pressure will be exerted and, as a result, the performance and life of the storage battery is adversely affected. Tests have shown that the ability of a separator of the present invention to recover its shape is so high as to improve the performance and life of the battery.

Example 2

As shown in Figure 1, five parts by weight of a glass fibre group 5 prepared by dipping 50% by weight of glass fibres 1 of a fibre diameter of 0.5 micron, 10% by weight of glass

fibres 2 of a fibre diameter of 6 microns and 40% by weight of glass fibres 3 of a fibre diameter of 11 microns in linseed oil of an iodine value of 170 which is a binder for binding fibres so as to deposit said oil on the surface and 95 parts by weight of a glass fibre group of the same rates of glass fibres on which no binder for binding fibres is deposited are uniformly dispersed at a rate of 0.5 part by weight of 100 parts by weight of water, are sheet-formed by an ordinary paper making technique and are dehydrated and dried to obtain a separator for storage batteries. Numerals 4, 5 and 6 indicate glass fibres having diameters respectively of 0.5, 6 and 11 microns on which no binder is deposited.

Example 3

60% by weight of glass fibres having a diameter of 0.5 micron, 36% by weight of glass fibres of a fibre diameter of 15 microns and 4% by weight of glass fibres of a fibre diameter of 11 microns having linseed oil deposited on the surface in advance are treated in the same manner as in Example 1 to produce a separator.

Table 2 shows various characteristics of Examples 1 and 2 as compared with those of the conventional one.

TABLE 2

Characteristics	Separators of the present invention		Conventional separator
	Example 1	Example 2	
Maximum pore diameter (microns)	13	12	23
Tensile strength (kg/cm^2)	15.7	18.4	2.5
Amount of retained electrolyte ($H_2SO_4^{c.c.}$/dry sepa.$^{c.c.}$)	2.0	2.2	3.1
Electrolyte retention (%)	98	98	95
Shape recovery (%)	92	93	70

Example 4

Fibres having an average length of 1, 3, 5, 10, 20, 50, 100, and 200 and a diameter of 6 microns are prepared in advance. 80% by weight of glass fibres having a diameter of 0.75 micron and 20% by weight of each of the above mentioned respective glass fibres are dispersed in water and are then treated in the same manner as in Example 1 to produce eight kinds of separators for storage batteries. Their tensile strengths and shape recoveries are plotted as the curves A in Figures 2 and 3.

Example 5

Respective glass fibres having average lengths of 1, 3, 5, 10, 20, 50, 100, and 200 mm and a diameter of 13 microns are prepared in advance. 85% by weight of glass fibres having a diameter of 0.5 micron and 15% by weight of each of the above mentioned respective fibres are dispersed in water and are then treated in the same manner as in Example 1 to produce eight kinds of separators. Their tensile strengths and shape recoveries are shown by curves B in Figures 2 and 3.

Example 6

The fibres of the same average lengths and diameters as in Example 3 are dispersed in the same amounts in water. On part by weight of natural cellulose made from Manila hemp is mixed in 100 parts by weight of the glass fibres to produce eight kinds of separators for storage batteries in the same manner as in Example 1. Their tensile strengths and shape recoveries are shown by curves C in Figures 2 and 3.

In the separators shown by curves A, B, and C, described above, when the average fibre length is less than 5 mm, no reinforcing effect is detected. It is well understood from Figure 2 that, when the average fibre length is 5 mm or larger, the mechanical strength of the separator is greatly improved, because, if the average fibre length is less than 5 mm, the number of entanglements with other glass fibres decreases and there is no reinforcing

effect. In the case of Figure 3, too, if the average fibre length is less than 5 mm, the shape recovery is considerably reduced.

Thus the separator of the present invention retains so much electrolyte and has such good electrolyte retention, that the performance and the life of this storage battery are much improved (as compared with conventional separators). Further, the separator is so strong that among other advantages, it is very easy to handle during assembly of the storage battery and is comparatively cheap.

WHAT WE CLAIM IS:-

1. A separator for storage batteries in the form of a sheet made by entangling together first glass having a diameter smaller than 1 micron as a base and second glass fibres having a diameter larger than 1 micron and an average fibre length of at least 5 mm.

2. A separator according to claim 1 wherein the first glass fibres are 50 to 95% by weight and the second glass fibres are 5 to 50% by weight.

3. A separator according to claim 1 wherein the second glass fibres include fibres having a diameter of 10 to 30 microns.

4. A separator according to claim 1 where the separator contains organic fibrous materials.

5. A separator according to claim 4 wherein the organic fibrous materials are natural fibrous materials.

6. A separator according to claim 4 wherein the organic fibrous materials are present in the amount of 0.1 to 5% by weight.

7. A separator according to claim 1 wherein the first glass fibres and second glass fibres are bound together by depositing a binder on the fibres in advance.

8. A separator according to claim 7 wherein the binder is made of an oil/fat.

9. A separator according to claim 7 wherein the amount of glass fibres on which the binder is deposited in advance is 0.1 to 40% by weight.

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1599077 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

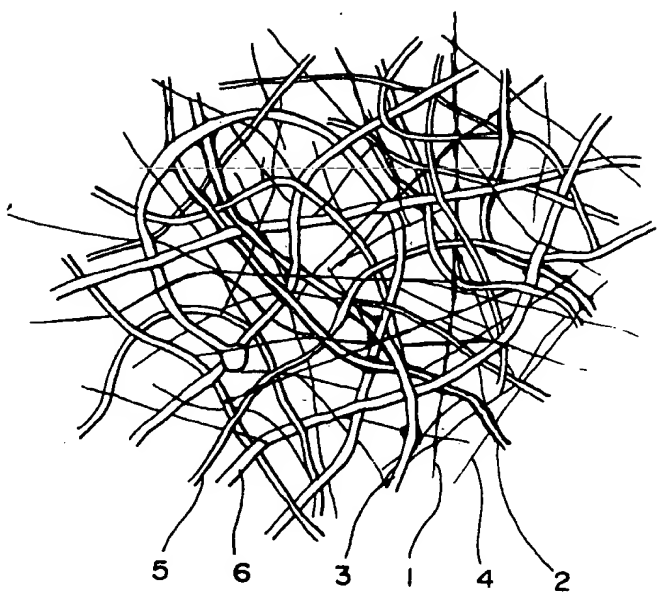

FIG. 1

1599077 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 2

FIG. 2

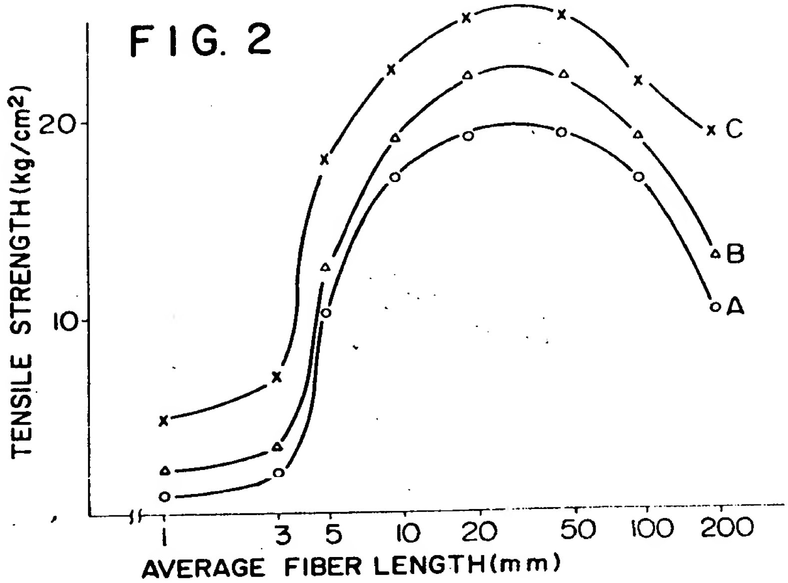

FIG. 3